

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-024328

(43)Date of publication of application : 27.01.1995

(51)Int.Cl.

B01J 31/06  
C02F 1/72

(21)Application number : 05-168138

(71)Applicant : SOKEN KAGAKU KK

(22)Date of filing : 07.07.1993

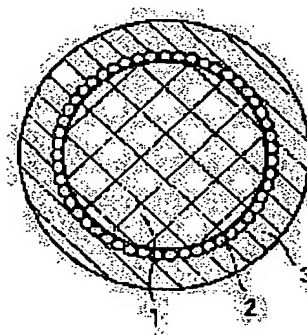
(72)Inventor : IMAI TATSUHIRO

## (54) CATALYST PARTICLE AND USE THEREOF

### (57)Abstract:

**PURPOSE:** To obtain a catalyst particle hardly lowered in catalytic activity and usable for a long time by providing a core material composed of a resin particle specified in its particle size, the metal oxide layer formed on the surface of the core material and the metal layer with a specific thickness formed on the metal oxide layer.

**CONSTITUTION:** A catalyst particle is constituted of a resin particle with a particle size of 0.05-5mm being a core material, the metal oxide layer 2 formed on the surface of the core material 1 and the metal layer 3 with a thickness of 0.01-5 $\mu$ m formed on the surface of the metal oxide layer 2. At that time, the wt. ratio of the resin particle and the metal oxide layer is set to the range of 99.9:0.1-90:10. A metal component selected from a group consisting of palladium, platinum, nickel, copper and an alloy based on at least one of those metals is added to the metal layer. This catalyst particle is used in the reaction in a gas-liquid mixed phase system, that is, oxidation reaction in water treatment, the reforming of petroleum for a fuel battery and the oxidation treatment reaction of dissolved gas.



## LEGAL STATUS

[Date of request for examination] 10.03.2000

[Date of sending the examiner's decision of rejection] 28.10.2003

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

**This Page Blank (uspic,**

---

## CLAIMS

---

### [Claim(s)]

[Claim 1] A resin particle with a particle diameter of 0.05–5mm which is a core material, and the metal oxide layer formed in the front face of this core material, It consists of a metal layer with a thickness of 0.01–5 micrometers formed in the front face of this metal oxide layer, and the weight ratio of this resin particle and the metallic oxide which forms a metal oxide layer is within the limits of 99.9:0.1–90:10. The catalyst particle characterized by containing the metal component chosen from the group which this metal layer becomes from the alloy which uses palladium, platinum, nickel, copper, and this at least one kind of metal as a principal component.

[Claim 2] The catalyst particle given in the 1st term of a claim characterized by a core material being an acrylic resin particle.

[Claim 3] The catalyst particle given in the 1st term of a claim characterized by a metallic oxide being an oxide of a quadrivalent metal.

[Claim 4] The 1st term of a claim characterized by being at least one kind of metallic oxide chosen from the group which a metallic oxide becomes from the tin oxide, silicon oxide, titanium oxide, and a zirconium dioxide, or a catalyst particle given in the 3rd term.

[Claim 5] The catalyst particle given in the 1st term of a claim characterized by a metal layer being a layer formed by the electroless deposition method.

[Claim 6] A resin particle with a particle diameter of 0.05–5mm which is a core material, and the metal oxide layer formed in the front face of this core material, It consists of a metal layer with a thickness of 0.01–5 micrometers formed in the front face of this metal oxide layer, and the weight ratio of this resin particle and the metallic oxide which forms a metal oxide layer is within the limits of 99.9:0.1–90:10. Operation of the catalyst particle characterized by reacting by the vapor–liquid mixed phase system under existence of the catalyst particle containing the metal component chosen from the group which this metal layer becomes from the alloy which uses palladium, platinum, nickel, copper, and this at least one kind of metal as a principal component.

[Claim 7] Operation of the catalyst particle given in the 6th term of a claim characterized by the reaction in a vapor–liquid mixed phase system being either oxidation treatment of the oxidation reaction in water treatment, hydrogen, or a nitride, the fixed reaction of a dissolved carbon dioxide, reforming of the petroleum for fuel

cells or an oxidation-treatment reaction of dissolved gas.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the new catalyst particle which has a granular gestalt, and this operation. It is related with the especially suitable catalyst particle for a reaction and this operation in a different interphase like [ it is still more detailed and ] a vapor-liquid mixed phase reaction in this invention.

[0002]

[Description of the Prior Art] There is a reaction of various phases, such as gaseous phase reaction, a liquid phase reaction, and a vapor-liquid mixed phase reaction, and industrially, in many cases, in order to react efficiently, the catalyst is used for the chemical reaction. By the heterogeneous catalytic reaction using a solid-state catalyst, a reaction rate etc. is remarkably changed by the contact nature of a reaction raw material and a catalyst among the reactions using such a catalyst.

[0003] Generally, since the whole reaction rate becomes large so that extent of contact in a catalyst and a reaction raw material is high, a chemical reaction makes the porosity matter support a catalyst, and enlarges the touch area of a catalyst and a reaction raw material. Such an approach is very effective at gaseous phase reaction and a liquid phase reaction, and much porosity support, such as a silica and an alumina, is already used.

[0004] However, at the reaction in the system intermingled in a gaseous phase and the liquid phase in the system of reaction like a vapor-liquid mixed phase reaction, in order that a reaction raw material may not invade even into the deep part of porosity support for the surface tension of air bubbles, even if it uses the above porosity support and enlarges surface area per unit volume, diffusion of a gaseous phase is blocked inside a catalyst particle, and the whole reaction rate does not improve so much. For example, as water-repellent porosity support is used for the catalyst used for JP,58-122046,A and a 62-38245 official report at a vapor-liquid mixed phase reaction and \*\*\*\* is not blockaded with waterdrop, the catalyst in the vapor-liquid mixed phase reaction which secured reactivity is indicated, and the reactivity of the catalyst in a vapor-liquid mixed phase reaction does not improve depending on only making specific surface area high like a general catalyst so that clearly from such a proposal.

[0005] It is necessary to drain, after oxidizing dissolved material and oxidizing [ in / general water treatment etc. / the request which is going to aim at reduction of environmental pollution is strong, and ], in order to reduce COD or a BOD value in recent years. The vapor-liquid mixed phase reaction is used and, moreover, it is necessary to process a lot of remarkable water at this vapor-liquid mixed phase reaction in oxidation treatment in such general water treatment. Therefore, at such a vapor-liquid mixed phase reaction, while it is required to use a catalyst with more high activity, it is necessary to carry out long duration maintenance of the activity as much as possible further.

[0006] As a catalyst of the reaction in such a vapor-liquid mixed phase system, invention of the art of the electrode water discharged from an electric-type deionized water manufacturing installation is indicated by JP,4-166215,A.

[0007] By this approach, by contacting the cathode water containing hydrogen gas, and the anode plate water containing oxygen gas, hydrogen gas and oxygen gas are made to react and water treatment is performed to the bottom of existence of the catalyst which made ion-exchange resin support palladium.

[0008] In such water treatment, very a lot of water must be processed, and since palladium is still more expensive, it is necessary to maintain the activity of a catalyst as much as possible for a long time.

[0009] Moreover, in order to raise the reactivity in a vapor-liquid mixed phase reaction, there are various proposals, such as an approach of improving the vapor-liquid mixed state in the system of reaction, (refer to official reports, such as JP,53-110968,A, 63-252540, JP,3-196832,A, and 4-156937). However, the attempt which is going to change the structure of the catalyst itself into these official reports, and is going to improve reactivity is not indicated.

[0010] By the way, in case a metal layer is formed by the electroless deposition method on this core material as a core material which consists of resin, in order to raise the wettability of a core material, the metallic-coating particle which has the approach and such structure which form a metal oxide layer on a core material is already known (for example, refer to JP,4-228503,A and a 4-183804 official report).

[0011] However, in these official reports, it is prepared in order that a metal oxide layer may improve the wettability of the core material at the time of forming a metal layer, and further, the use as a coating, adhesives, powder metallurgy, injection molding, an electromagnetic shielding material, dispersion-strengthening material, an electrostatography toner, powder coatings, cosmetics, etc. is only proposed, and these metallic-coating particles are not examined at all about the application as a

catalyst.

[0012] this invention person acquires knowledge that the catalysis is maintained for a long period of time, and came to complete this invention while he had the catalysis excellent in the particle which has the metal layer formed in the resin core material front face from the specific metal through the metal oxide layer as a result of examining many things in the field of a catalyst which did not inquire at all conventionally about such a metallic-coating particle.

[0013]

[Objects of the Invention] This invention aims at offering the approach of using the catalyst particle and its catalyst particle of a new gestalt. This invention aims still more detailed at offering the approach of using the catalyst particle which can be used for a long time that catalytic activity cannot fall easily, and this catalyst particle.

[0014]

[Summary of the Invention] A resin particle with a mean particle diameter of 0.05–5mm whose catalyst particle of this invention is a core material, It consists of a metal oxide layer formed in the front face of this core material, and a metal layer with a thickness of 0.01–5 micrometers formed in the front face of this metal oxide layer. The weight ratio of this resin particle and the metallic oxide which forms a metal oxide layer is within the limits of 99.9:0.1–90:10. It is characterized by containing the metal component chosen from the group which this metal layer becomes from the alloy which uses palladium, platinum, nickel, copper, and this at least one kind of metal as a principal component.

[0015] Moreover, a resin particle with a mean particle diameter of 0.05–5mm whose operation of the catalyst particle of this invention is a core material, It consists of a metal oxide layer formed in the front face of this core material, and a metal layer with a thickness of 0.01–5 micrometers formed in the front face of this metal oxide layer. The weight ratio of this resin particle and the metallic oxide which forms a metal oxide layer is within the limits of 99.9:0.1–90:10. It is characterized by reacting by the vapor-liquid mixed phase system under existence of the catalyst particle containing the metal component chosen from the group which this metal layer becomes from the alloy which uses palladium, platinum, nickel, copper, and this at least one kind of metal as a principal component.

[0016] The catalyst particle of this invention has the cross-section structure where the laminating of a metal oxide layer and the metal layer was carried out to the front face of a resin particle in this sequence as mentioned above. Thus, catalytic activity stops being able to fall easily with time by forming the thin layer which consists of a

metallic oxide on the surface of a core material, and forming a metal layer on this metal oxide layer further.

[0017] Moreover, since the resin particle is used as a core material, the specific gravity of this catalyst particle becomes low, and in using it without fixing this catalyst like the moving bed or the fluid bed, the distribution to the system of reaction becomes very easy.

[0018] Especially the catalyst particle of this invention has high usefulness as a catalyst in the reaction catalyst in a vapor-liquid mixed phase system, a vapor-liquid mixed phase reaction, and the vapor-liquid mixed phase reaction either [ at least / whose ] a raw material system or a product is a gas or a liquid in more detail.

[0019]

[Detailed Description of the Invention] Next, the catalyst particle of this invention and its operation are explained concretely. The catalyst particle of this invention consists of a core material 1, a metal oxide layer 2 formed in this core material 1 front face, and a metal layer 3 formed on this metal oxide layer 2, as shown in drawing 1.

[0020] In the catalyst particle of this invention, the core material is formed from resin. This core material has the desirable resin particle which has the mean particle diameter within the limits of 0.05-5mm, and has the mean particle diameter of further 0.1-5mm, and especially its resin particle that has the mean particle diameter which is 0.2-2mm is desirable. Since radius of curvature does not become not much small, the resin particle which has the above mean particle diameter can form a uniform metal layer in this resin particle front face easily for example, by the electroless deposition method.

[0021] As an example of the resin which forms this core material, acrylic (meta) resin, styrene resin, styrene / (meta) acrylic resin, polyethylene system resin, a polypropylene resin, ABS plastics, an AS resin, polyacetal resin, polycarbonate system resin, phenol system resin, benzoguanamine system resin, epoxy system resin, polyester system resin, polyamide system resin, urethane system resin, and polyimide system resin can be mentioned. This organic polymer may be any of the cross linked polymer or the non-cross linked polymer. Acrylic resin like acrylic resin (example: methyl methacrylate), and styrene / (meta) acrylic resin (meta) also in these is desirable.

[0022] Thus, while the specific gravity of the catalyst particle of this invention becomes low and the distribution to the system of reaction becomes easy by using a resin particle as a core material, catalytic activity is maintainable from the case where a glass bead etc. is used, for example as a core material for a long time.

[0023] The metal oxide layer is formed in the above core material front faces at the catalyst particle of this invention. This metal oxide layer is usually formed from the oxide of a quadrivalent metal, and can mention the tin oxide, silicon oxide, titanium oxide, and a zirconium dioxide as a suitable example of the oxide of such a quadrivalent metal. As a metallic oxide, 0.001–1 micrometer of particles which have the mean particle diameter of 0.02–0.1 micrometers preferably is usually used here. That is, 1 of the resin particle which is a core material / metallic-oxide particle which has 1 / about 10,000 to 1/5,000 mean particle diameter preferably 5,000,000 to about 1/50 is usually used.

[0024] This metal oxide layer can form a resin particle and metallic-oxide powder by the dry-blending method (the dryblend method, mechanochemical law) using mixers, such as a ball mill. The approach using particle compound-sized equipments, such as a hybridization system (made in the Nara, Inc. machine factory), a mechano fusion system (Hosokawa Micron CORP. make), and cosmos (Kawasaki Heavy Industries, Ltd. make), as an example of a dry-blending method can be mentioned here. A metal oxide layer with a high continuity can be formed in a resin particle front face by mixing a resin particle and a metallic-oxide particle by such dry-blending method.

[0025] Furthermore, if melting kneading is carried out at an ununiformity and resin and a metallic oxide are ground after that, the resin particle by which the metallic oxide was fixed to the front face will be obtained. When a metallic oxide besides the above-mentioned approach is insoluble to water and a monomer, or refractory, in order that a metallic oxide may act as a distributed stabilizer by making an aqueous solvent distribute this metallic-oxide particle, and putting in and carrying out the suspension polymerization of the monomer into this aqueous solvent, the resin particle by which the metallic oxide was fixed to the front face is obtained carrying out a polymerization. Thus, by carrying out a polymerization, most forms a thin layer in a resin particle front face according to the interface operation, it is fixed, and a metallic oxide forms a uniform metal oxide layer.

[0026] The metal oxide layer formed [ especially ] with particle compound-sized equipment by this invention and the metal oxide layer formed by blending and carrying out the polymerization of the metallic oxide in the case of a suspension polymerization are desirable.

[0027] Thus, by forming a metal layer through a metal oxide layer on a resin core material, catalytic activity is maintainable for a long time. And a homogeneous high metal layer can be easily formed, for example by the electroless deposition method.

[0028] The catalyst particle of this invention has the metal layer on the



above-mentioned metal oxide layer. This metal layer is formed with the metal which has a catalysis, and is a metal other than the metal in a metal oxide layer.

[0029] As a metal which has such a catalysis, the alloy which contains palladium, platinum, nickel, copper, and these metals as a principal component can be mentioned. That is, this metal layer may be formed by the metal independent of either palladium, platinum, nickel or copper, and may be the alloy of these metals. Furthermore, in this metal layer, other components may contain within limits by which a catalysis is not spoiled. Here, as an example of other components which can form a metal layer with the above-mentioned metal or an alloy, B, P, Co, Fe, Ag, Au, Rh, Ru, Cr, Cd, Pb, Sn, Zn, W, In, and Ir can be mentioned. Such other components can contain usual in 4 or less % of the weight of an amount still more preferably 13 or less % of the weight preferably 25 or less % of the weight in a metal layer.

[0030] Although this metal layer can be formed with a vacuum deposition method, the sputtering method, PVD, a CVD method, etc., it is desirable especially to form by the electroless deposition method by this invention.

[0031] An electroless deposition method is an approach of depositing a metal, without passing a current by adding a reducing agent to the water solution containing a metal ion, and warming thru/or heating, and, as for the metal layer formed by this electroless deposition method, homogeneity becomes high very much.

[0032] The metal layer has 0.01–5-micrometer average thickness, and it is desirable that it is in within the limits this average thickness of whose is 0.1–1.5 micrometers further. Moreover, the weight ratio of the metal which forms this metal layer, and the metallic oxide which forms said metal oxide layer is within the limits of 99.9:0.1–90:10. By using a metal and a metallic oxide in the above amount, long duration maintenance of the activity of a catalyst is carried out.

[0033] After this metal layer forms a metal oxide layer on the surface of a core material as mentioned above, it usually performs induction-ized processing and activation, and, subsequently forms a metal layer by the electroless deposition method. Induction-ized processing is processing immersed in the 1st tin solution of hydrochloric acid of chlorination etc. in a plated object here, and activation is processing immersed in the palladium-chloride solution of hydrochloric acid etc. in the induction--ization-processed plated object.

[0034] In this way, a metal layer can be formed by supplying the core material in which the plated body with which induction-ized processing and activation were performed, i.e., a metal oxide layer, was formed in the electroless deposition liquid maintained by the temperature of room temperature –90 degree C within the limits, and making it

react to the bottom of stirring for 10 minutes to 24 hours.

[0035] Since the resin particle is used for the catalyst particle of this invention as a core material as mentioned above, specific gravity becomes low and distribution of the catalyst particle to the system of reaction becomes easy. The activity of a catalyst particle can be maintained still in this way for a long time by forming the metal layer which serves as a catalyst through a metal oxide layer further, using a resin particle as a core material. When a resin core material and a metal oxide layer work together mutually shows that catalytic activity has stopped being able to fall easily so that clearly [ there are few falls of catalytic activity in the catalyst particle of this invention, and / it may mention later and ] from contrast with an example and the example of a comparison, although the device about what is done for the long duration maintenance of the activity is not clear.

[0036] Although the catalyst particle of this invention has the catalytic activity over various reactions and it can be used for it according to the class of metal which forms the metal layer in a front face as the catalyst in a single phase like a liquid phase reaction and gaseous phase reaction, especially an oxidation catalyst, it is suitable as a catalyst of the reaction which advances by especially different interphase. As an example of the reaction which advances by such different interphase, either [ at least ] a raw material system or a product can mention the vapor-liquid mixed phase reaction which is a gas or a liquid. The catalyst particle of this invention has still higher usefulness as an oxidation catalyst in such a vapor-liquid mixed phase reaction.

[0037] As an example of such a vapor-liquid mixed phase reaction, oxidation treatment of the oxidation reaction in water treatment, hydrogen, or a nitride, the fixed reaction of a dissolved carbon dioxide, reforming of the petroleum for fuel cells, the oxidation-treatment reaction of dissolved gas, oxidation reaction of aldehydes, oxidation reaction of alcohols, and the dehydrogenation of alcohols can be mentioned. The catalyst particle of this invention has the high usefulness as an oxidation catalyst in reforming of oxidation treatment of the oxidation reaction in water treatment, hydrogen, or a nitride, the fixed reaction of a dissolved carbon dioxide, and the petroleum for fuel cells, and the oxidation-treatment reaction of dissolved gas also in these.

[0038] The example of oxidation treatment of the water which contains the hydrazine which is a nitride in drawing 2 is shown. the treated water which contains a hydrazine from a tank 11 -- the liquid-sending pump 12 -- the processing from the lower limit section -- it introduces into a column 13. this -- another -- air -- Blois 14 -- the same -- processing -- from the lower limit section of a column 13 -- introducing --

processing -- treated water and air are mixed in a column 13. this processing -- in the column 13, it fills up with the catalyst particle of this invention to which the laminating of a silicon oxide layer and the palladium layer was carried out in this sequence on the front face of an acrylic resin core material, and this catalyst particle, said treated water, and air contact in the state of a vapor-liquid mixed phase. As for this treated water and air, it is desirable to contact a catalyst particle by upward flow. Thus, by processing, oxidative degradation of the hydrazine is carried out, it becomes nitrogen and water, and is discharged from an exhaust port 15. In addition, it is the mean flow-time in the oxidative degradation of this hydrazine for 0.1 - 5 minutes, and reaction temperature is usually 30-80 degrees C.

[0039] In a vapor-liquid mixed phase reaction as shown in the example of oxidation treatment of the water containing the above-mentioned hydrazine, long duration maintenance of the catalytic activity of the catalyst particle of this invention is carried out very much. That is, although the catalytic activity of the time of reaction initiation falls very much for a short time by the particle which formed the metal oxide layer in front faces, such as a glass bead, and formed the direct metal layer in the front face of the particle which prepared the metal layer on this metal oxide layer, or a resin particle, without using a resin particle as a core material, the catalyst particle of this invention has many which catalytic activity cannot fall easily and have twice [ more than ] as many catalytic activity as the above particles.

[0040] The catalyst particle of this invention does so effectiveness equivalent to the above-mentioned example not only in oxidation treatment of a hydrazine but in various vapor-liquid mixed phase reactions. In above-mentioned drawing 2 , for example, instead of the treated water containing a hydrazine Hydrogen can be oxidized by throwing in the liquid with which hydrogen gas is dissolved in the tank 11. Moreover, reforming of the petroleum for fuel cells can be performed by throwing in the petroleum raw material for fuel cells. By throwing in the seawater where the carbon dioxide is furthermore dissolved, immobilization and reforming of a carbon dioxide can be performed, and this gas can be oxidized by throwing in the liquid which absorbed gas with the gas absorption scrubber.

[0041] Moreover, the absorption and oxidation of gas in this wetted wall column can be performed to coincidence by forming the wall material of a wetted wall column using the catalyst particle of this invention. Furthermore, the catalyst particle of this invention usually has about three 1.2 - 2.5 g/cm specific gravity, and since it approximates with the specific gravity of processing liquid, for example, in case this specific gravity uses this catalyst by the moving bed or the fluid bed in a vapor-liquid

mixing phase style, it can contact a catalyst particle and processing liquid effectively.  
[0042]

[Effect of the Invention] By the catalyst particle of this invention, since it has a metal oxide layer on the core material which consists of a resin particle, and this core material front face and the metal layer is formed on this metal oxide layer, in the reaction in the interphase which meets a different phase, especially the oxidation reaction in a vapor-liquid mixed phase, period maintenance of the effective catalytic activity is carried out over a long period of time.

[0043] Moreover, since a core material consists of a resin particle, this catalyst particle has low specific gravity, and has the liquid which it is going to make react, and the approximated specific gravity. The processing matter and a catalyst particle can be effectively contacted by following, for example, using the catalyst particle of this invention.

[0044] Especially the catalyst particle of this invention has high usefulness as a reaction catalyst in a vapor-liquid mixed phase.

[0045]

[Example] Next, although an example is shown and this invention is explained, thereby, this invention is not limited.

[0046]

[The example 1 of manufacture] The water 1400 weight section was taught into the polymerization container with a capacity [ made from stainless steel ] of 5l. which has stirring equipment, a thermometer, and nitrogen gas installation tubing. Subsequently, after dissolving the polyvinyl alcohol 3.3 weight section in this water, the methyl methacrylate 600 weight section which dissolved the benzoyl peroxide 6 weight section in this solution was added, it heated at 75 degrees C under the certain stirring conditions carried out slowly for 5 hours, and the suspension polymerization was made to complete.

[0047] Rinsing desiccation of the obtained suspension was carried out after centrifugal hydroextraction, and polymethylmethacrylate fine particles with a mean particle diameter of 200 micrometers were obtained.

[0048]

[The example 2 of manufacture] In the example 1 of manufacture, instead of the water 1400 weight section, the suspension polymerization was performed similarly and fine particles with a mean particle diameter of 200 micrometers were obtained except having taught the water 1400 weight section and the silicon oxide 18 weight section.

[0049] When the obtained fine particles were observed with the scanning electron

microscope, the particle front faces were the polymethylmethacrylate fine particles covered with silicon oxide.

[0050]

[The example 3 of manufacture] 100g of polymethylmethacrylate fine particles and 3g of silicon oxide obtained in the example 1 of manufacture were put into the commercial capacity Pori bottle of 500 cc, rotational speed was adjusted so that the rotational frequency of the Pori bottle might be set to 60 ppm, and it processed for 60 minutes.

[0051] When the obtained fine particles were observed with the scanning electron microscope, they were the polymethylmethacrylate fine particles covered with the silicon oxide same with having been obtained in the example 1 of manufacture.

[0052]

[The example 1 of a comparison] After immersing the fine particles obtained in the example 1 of manufacture in the 1st tin solution of hydrochloric acid of chlorination and performing induction-ized processing, it was immersed in the palladium-chloride solution of hydrochloric acid, and activation was performed.

[0053] Subsequently, the plating liquid which consists of 32g [ of palladium chlorides ], 400g [ of 25% aqueous ammonia ], 68g [ of disodium ethylenediaminetetraacetate ], and hydrazine 5.8g and 600g of ion exchange water in 50g of processing fine particles performed electroless deposition over 1 hour at 40 degrees C. Then, centrifugal hydroextraction was carried out, rinsing desiccation was carried out and the palladium plating particle was obtained. The thickness of the palladium layer of the obtained plating particle was 1.1 micrometers.

[0054] Although the hydrazinolysis rate immediately after reaction initiation was high as it was shown in Table 1 with the hydrazinolysis ability measuring device shown in drawing 2 using the obtained fine particles, when the catabolic rate of a hydrazine was measured, catalytic activity fell for a short time, and it stopped showing effective catalytic activity practical after 24-hour progress. A result is shown in Table 1.

[0055]

[Example 1] After immersing the fine particles obtained in the example 2 of manufacture in the 1st tin solution of hydrochloric acid of chlorination and performing induction-ized processing, it was immersed in the palladium-chloride solution of hydrochloric acid, and activation was performed.

[0056] Subsequently, the plating liquid which consists of 32g [ of palladium chlorides ], 400g [ of 25% aqueous ammonia ], 68g [ of disodium ethylenediaminetetraacetate ], and hydrazine 5.8g and 600g of ion exchange water in 50g of processing fine particles

performed electroless deposition over 1 hour at 40 degrees C.

[0057] Then, centrifugal hydroextraction was carried out, rinsing desiccation was carried out and the palladium plating particle was obtained. The thickness of the palladium layer of the obtained plating particle was 1.1 micrometers. With the hydrazinolysis ability measuring device shown in drawing 2 using the obtained fine particles, when the catabolic rate of a hydrazine was measured, as shown in Table 1, there is almost no difference between the catalytic activity of 24-hour progress, and the catalytic activity after 28-day progress, and this catalyst was able to be used for it for a long period of time. A result is shown in Table 1.

[0058]

[Example 2] After immersing the fine particles obtained in the example 3 of manufacture in the 1st tin solution of hydrochloric acid of chlorination and performing induction-ized processing, it was immersed in the palladium-chloride solution of hydrochloric acid, and activation was performed.

[0059] Subsequently, the plating liquid which consists of 32g [ of palladium chlorides ], 400g [ of 25% aqueous ammonia ], 68g [ of disodium ethylenediaminetetraacetate ], and hydrazine 5.8g and 600g of ion exchange water in 50g of processing fine particles performed electroless deposition over 1 hour at 40 degrees C.

[0060] Then, centrifugal hydroextraction was carried out, rinsing desiccation was carried out and the palladium plating particle was obtained. The thickness of the palladium layer of the obtained plating particle was 1.1 micrometers. With the hydrazinolysis ability measuring device shown in drawing 2 using the obtained fine particles, when the catabolic rate of a hydrazine was measured, as shown in Table 1, there is almost no difference between the catalytic activity of 24-hour progress, and the catalytic activity after 28-day progress, and this catalyst was able to be used for it for a long period of time. A result is shown in Table 1.

[0061]

[The example 2 of a comparison] In the example 1, the catalyst particle was similarly manufactured instead of the fine particles obtained in the example 2 of manufacture except having used the commercial glass bead (mean particle diameter of 0.2mm).

[0062] Although the catabolic rate of a hydrazine was measured like the example 1 using this catalyst particle, the catabolic rate immediately after reaction initiation is not so high, either, and since it became below the catabolic rate of the example 1 of a comparison 24 more hours after, the reaction was stopped in this phase. A result is shown in Table 1.

[0063]

---

TECHNICAL PROBLEM

---

[Description of the Prior Art] There is a reaction of various phases, such as gaseous phase reaction, a liquid phase reaction, and a vapor-liquid mixed phase reaction, and industrially, in many cases, in order to react efficiently, the catalyst is used for the chemical reaction. By the heterogeneous catalytic reaction using a solid-state catalyst, a reaction rate etc. is remarkably changed by the contact nature of a reaction raw material and a catalyst among the reactions using such a catalyst.

[0003] Generally, since the whole reaction rate becomes large so that extent of contact in a catalyst and a reaction raw material is high, a chemical reaction makes the porosity matter support a catalyst, and enlarges the touch area of a catalyst and a reaction raw material. Such an approach is very effective at gaseous phase reaction and a liquid phase reaction, and much porosity support, such as a silica and an alumina, is already used.

[0004] However, at the reaction in the system intermingled in a gaseous phase and the liquid phase in the system of reaction like a vapor-liquid mixed phase reaction, in order that a reaction raw material may not invade even into the deep part of porosity support for the surface tension of air bubbles, even if it uses the above porosity support and enlarges surface area per unit volume, diffusion of a gaseous phase is blocked inside a catalyst particle, and the whole reaction rate does not improve so much. For example, as water-repellent porosity support is used for the catalyst used for JP,58-122046,A and a 62-38245 official report at a vapor-liquid mixed phase reaction and \*\*\*\* is not blockaded with waterdrop, the catalyst in the vapor-liquid mixed phase reaction which secured reactivity is indicated, and the reactivity of the catalyst in a vapor-liquid mixed phase reaction does not improve depending on only making specific surface area high like a general catalyst so that clearly from such a proposal.

[0005] It is necessary to drain, after oxidizing dissolved material and oxidizing [ in / general water treatment etc. / the request which is going to aim at reduction of environmental pollution is strong, and ], in order to reduce COD or a BOD value in recent years. The vapor-liquid mixed phase reaction is used and, moreover, it is necessary to process a lot of remarkable water at this vapor-liquid mixed phase reaction in oxidation treatment in such general water treatment. Therefore, at such a vapor-liquid mixed phase reaction, while it is required to use a catalyst with more high

activity, it is necessary to carry out long duration maintenance of the activity as much as possible further.

[0006] As a catalyst of the reaction in such a vapor-liquid mixed phase system, invention of the art of the electrode water discharged from an electric-type deionized water manufacturing installation is indicated by JP,4-166215,A.

[0007] By this approach, by contacting the cathode water containing hydrogen gas, and the anode plate water containing oxygen gas, hydrogen gas and oxygen gas are made to react and water treatment is performed to the bottom of existence of the catalyst which made ion-exchange resin support palladium.

[0008] In such water treatment, very a lot of water must be processed, and since palladium is still more expensive, it is necessary to maintain the activity of a catalyst as much as possible for a long time.

[0009] Moreover, in order to raise the reactivity in a vapor-liquid mixed phase reaction, there are various proposals, such as an approach of improving the vapor-liquid mixed state in the system of reaction, (refer to official reports, such as JP,53-110968,A, 63-252540, JP,3-196832,A, and 4-156937). However, the attempt which is going to change the structure of the catalyst itself into these official reports, and is going to improve reactivity is not indicated.

[0010] By the way, in case a metal layer is formed by the electroless deposition method on this core material as a core material which consists of resin, in order to raise the wettability of a core material, the metallic-coating particle which has the approach and such structure which form a metal oxide layer on a core material is already known (for example, refer to JP,4-228503,A and a 4-183804 official report).

[0011] However, in these official reports, it is prepared in order that a metal oxide layer may improve the wettability of the core material at the time of forming a metal layer, and further, the use as a coating, adhesives, powder metallurgy, injection molding, an electromagnetic shielding material, dispersion-strengthening material, an electrostatography toner, powder coatings, cosmetics, etc. is only proposed, and these metallic-coating particles are not examined at all about the application as a catalyst.

[0012] this invention person acquires knowledge that the catalysis is maintained for a long period of time, and came to complete this invention while he had the catalysis excellent in the particle which has the metal layer formed in the resin core material front face from the specific metal through the metal oxide layer as a result of examining many things in the field of a catalyst which did not inquire at all conventionally about such a metallic-coating particle.



[0013]

[Objects of the Invention] This invention aims at offering the approach of using the catalyst particle and its catalyst particle of a new gestalt. This invention aims still more detailed at offering the approach of using the catalyst particle which can be used for a long time that catalytic activity cannot fall easily, and this catalyst particle.

[0014]

[Summary of the Invention] A resin particle with a mean particle diameter of 0.05–5mm whose catalyst particle of this invention is a core material, It consists of a metal oxide layer formed in the front face of this core material, and a metal layer with a thickness of 0.01–5 micrometers formed in the front face of this metal oxide layer. The weight ratio of this resin particle and the metallic oxide which forms a metal oxide layer is within the limits of 99.9:0.1–90:10. It is characterized by containing the metal component chosen from the group which this metal layer becomes from the alloy which uses palladium, platinum, nickel, copper, and this at least one kind of metal as a principal component.

[0015] Moreover, a resin particle with a mean particle diameter of 0.05–5mm whose operation of the catalyst particle of this invention is a core material, It consists of a metal oxide layer formed in the front face of this core material, and a metal layer with a thickness of 0.01–5 micrometers formed in the front face of this metal oxide layer. The weight ratio of this resin particle and the metallic oxide which forms a metal oxide layer is within the limits of 99.9:0.1–90:10. It is characterized by reacting by the vapor–liquid mixed phase system under existence of the catalyst particle containing the metal component chosen from the group which this metal layer becomes from the alloy which uses palladium, platinum, nickel, copper, and this at least one kind of metal as a principal component.

[0016] The catalyst particle of this invention has the cross–section structure where the laminating of a metal oxide layer and the metal layer was carried out to the front face of a resin particle in this sequence as mentioned above. Thus, catalytic activity stops being able to fall easily with time by forming the thin layer which consists of a metallic oxide on the surface of a core material, and forming a metal layer on this metal oxide layer further.

[0017] Moreover, since the resin particle is used as a core material, the specific gravity of this catalyst particle becomes low, and in using it without fixing this catalyst like the moving bed or the fluid bed, the distribution to the system of reaction becomes very easy.

[0018] Especially the catalyst particle of this invention has high usefulness as a

catalyst in the reaction catalyst in a vapor-liquid mixed phase system, a vapor-liquid mixed phase reaction, and the vapor-liquid mixed phase reaction either [ at least / whose ] a raw material system or a product is a gas or a liquid in more detail.

[0019]

[Detailed Description of the Invention] Next, the catalyst particle of this invention and its operation are explained concretely. The catalyst particle of this invention consists of a core material 1, a metal oxide layer 2 formed in this core material 1 front face, and a metal layer 3 formed on this metal oxide layer 2, as shown in drawing 1 .

[0020] In the catalyst particle of this invention, the core material is formed from resin. This core material has the desirable resin particle which has the mean particle diameter within the limits of 0.05-5mm, and has the mean particle diameter of further 0.1-5mm, and especially its resin particle that has the mean particle diameter which is 0.2-2mm is desirable. Since radius of curvature does not become not much small, the resin particle which has the above mean particle diameter can form a uniform metal layer in this resin particle front face easily for example, by the electroless deposition method.

[0021] As an example of the resin which forms this core material, acrylic (meta) resin, styrene resin, styrene / (meta) acrylic resin, polyethylene system resin, a polypropylene resin, ABS plastics, an AS resin, polyacetal resin, polycarbonate system resin, phenol system resin, benzoguanamine system resin, epoxy system resin, polyester system resin, polyamide system resin, urethane system resin, and polyimide system resin can be mentioned. This organic polymer may be any of the cross linked polymer or the non-cross linked polymer. Acrylic resin like acrylic resin (example: methyl methacrylate), and styrene / (meta) acrylic resin (meta) also in these is desirable.

[0022] Thus, while the specific gravity of the catalyst particle of this invention becomes low and the distribution to the system of reaction becomes easy by using a resin particle as a core material, catalytic activity is maintainable from the case where a glass bead etc. is used, for example as a core material for a long time.

[0023] The metal oxide layer is formed in the above core material front faces at the catalyst particle of this invention. This metal oxide layer is usually formed from the oxide of a quadrivalent metal, and can mention the tin oxide, silicon oxide, titanium oxide, and a zirconium dioxide as a suitable example of the oxide of such a quadrivalent metal. As a metallic oxide, 0.001-1 micrometer of particles which have the mean particle diameter of 0.02-0.1 micrometers preferably is usually used here. That is, 1 of the resin particle which is a core material / metallic-oxide particle which

has 1 / about 10,000 to 1/5,000 mean particle diameter preferably 5,000,000 to about 1/50 is usually used.

[0024] This metal oxide layer can form a resin particle and metallic-oxide powder by the dry-blending method (the dryblend method, mechanochemical law) using mixers, such as a ball mill. The approach using particle compound-ized equipments, such as a hybridization system (made in the Nara, Inc. machine factory), a mechano fusion system (Hosokawa Micron CORP. make), and cosmos (Kawasaki Heavy Industries, Ltd. make), as an example of a dry-blending method can be mentioned here. A metal oxide layer with a high continuity can be formed in a resin particle front face by mixing a resin particle and a metallic-oxide particle by such dry-blending method.

[0025] Furthermore, if melting kneading is carried out at an ununiformity and resin and a metallic oxide are ground after that, the resin particle by which the metallic oxide was fixed to the front face will be obtained. When a metallic oxide besides the above-mentioned approach is insoluble to water and a monomer, or refractory, in order that a metallic oxide may act as a distributed stabilizer by making an aqueous solvent distribute this metallic-oxide particle, and putting in and carrying out the suspension polymerization of the monomer into this aqueous solvent, the resin particle by which the metallic oxide was fixed to the front face is obtained carrying out a polymerization. Thus, by carrying out a polymerization, most forms a thin layer in a resin particle front face according to the interface operation, it is fixed, and a metallic oxide forms a uniform metal oxide layer.

[0026] The metal oxide layer formed [ especially ] with particle compound-ized equipment by this invention and the metal oxide layer formed by blending and carrying out the polymerization of the metallic oxide in the case of a suspension polymerization are desirable.

[0027] Thus, by forming a metal layer through a metal oxide layer on a resin core material, catalytic activity is maintainable for a long time. And a homogeneous high metal layer can be easily formed, for example by the electroless deposition method.

[0028] The catalyst particle of this invention has the metal layer on the above-mentioned metal oxide layer. This metal layer is formed with the metal which has a catalysis, and is a metal other than the metal in a metal oxide layer.

[0029] As a metal which has such a catalysis, the alloy which contains palladium, platinum, nickel, copper, and these metals as a principal component can be mentioned. That is, this metal layer may be formed by the metal independent of either palladium, platinum, nickel or copper, and may be the alloy of these metals. Furthermore, in this metal layer, other components may contain within limits by which a catalysis is not

spoiled. Here, as an example of other components which can form a metal layer with the above-mentioned metal or an alloy, B, P, Co, Fe, Ag, Au, Rh, Ru, Cr, Cd, Pb, Sn, Zn, W, In, and Ir can be mentioned. Such other components can contain usual in 4 or less % of the weight of an amount still more preferably 13 or less % of the weight preferably 25 or less % of the weight in a metal layer.

[0030] Although this metal layer can be formed with a vacuum deposition method, the sputtering method, PVD, a CVD method, etc., it is desirable especially to form by the electroless deposition method by this invention.

[0031] An electroless deposition method is an approach of depositing a metal, without passing a current by adding a reducing agent to the water solution containing a metal ion, and warming thru/or heating, and, as for the metal layer formed by this electroless deposition method, homogeneity becomes high very much.

[0032] The metal layer has 0.01–5-micrometer average thickness, and it is desirable that it is in within the limits this average thickness of whose is 0.1–1.5 micrometers further. Moreover, the weight ratio of the metal which forms this metal layer, and the metallic oxide which forms said metal oxide layer is within the limits of 99.9:0.1–90:10. By using a metal and a metallic oxide in the above amount, long duration maintenance of the activity of a catalyst is carried out.

[0033] After this metal layer forms a metal oxide layer on the surface of a core material as mentioned above, it usually performs induction-ized processing and activation, and, subsequently forms a metal layer by the electroless deposition method. Induction-ized processing is processing immersed in the 1st tin solution of hydrochloric acid of chlorination etc. in a plated object here, and activation is processing immersed in the palladium-chloride solution of hydrochloric acid etc. in the induction--ization-processed plated object.

[0034] In this way, a metal layer can be formed by supplying the core material in which the plated body with which induction-ized processing and activation were performed, i.e., a metal oxide layer, was formed in the electroless deposition liquid maintained by the temperature of room temperature –90 degree C within the limits, and making it react to the bottom of stirring for 10 minutes to 24 hours.

[0035] Since the resin particle is used for the catalyst particle of this invention as a core material as mentioned above, specific gravity becomes low and distribution of the catalyst particle to the system of reaction becomes easy. The activity of a catalyst particle can be maintained still in this way for a long time by forming the metal layer which serves as a catalyst through a metal oxide layer further, using a resin particle as a core material. When a resin core material and a metal oxide layer work together

mutually shows that catalytic activity has stopped being able to fall easily so that clearly [ there are few falls of catalytic activity in the catalyst particle of this invention, and / it may mention later and ] from contrast with an example and the example of a comparison, although the device about what is done for the long duration maintenance of the activity is not clear.

[0036] Although the catalyst particle of this invention has the catalytic activity over various reactions and it can be used for it according to the class of metal which forms the metal layer in a front face as the catalyst in a single phase like a liquid phase reaction and gaseous phase reaction, especially an oxidation catalyst, it is suitable as a catalyst of the reaction which advances by especially different interphase. As an example of the reaction which advances by such different interphase, either [ at least ] a raw material system or a product can mention the vapor-liquid mixed phase reaction which is a gas or a liquid. The catalyst particle of this invention has still higher usefulness as an oxidation catalyst in such a vapor-liquid mixed phase reaction.

[0037] As an example of such a vapor-liquid mixed phase reaction, oxidation treatment of the oxidation reaction in water treatment, hydrogen, or a nitride, the fixed reaction of a dissolved carbon dioxide, reforming of the petroleum for fuel cells, the oxidation-treatment reaction of dissolved gas, oxidation reaction of aldehydes, oxidation reaction of alcohols, and the dehydrogenation of alcohols can be mentioned. The catalyst particle of this invention has the high usefulness as an oxidation catalyst in reforming of oxidation treatment of the oxidation reaction in water treatment, hydrogen, or a nitride, the fixed reaction of a dissolved carbon dioxide, and the petroleum for fuel cells, and the oxidation-treatment reaction of dissolved gas also in these.

[0038] The example of oxidation treatment of the water which contains the hydrazine which is a nitride in drawing 2 is shown. the treated water which contains a hydrazine from a tank 11 -- the liquid-sending pump 12 -- the processing from the lower limit section -- it introduces into a column 13. this -- another -- air -- Blois 14 -- the same -- processing -- from the lower limit section of a column 13 -- introducing -- processing -- treated water and air are mixed in a column 13. this processing -- in the column 13, it fills up with the catalyst particle of this invention to which the laminating of a silicon oxide layer and the palladium layer was carried out in this sequence on the front face of an acrylic resin core material, and this catalyst particle, said treated water, and air contact in the state of a vapor-liquid mixed phase. As for this treated water and air, it is desirable to contact a catalyst particle by upward flow. Thus, by processing, oxidative degradation of the hydrazine is carried out, it becomes nitrogen

and water, and is discharged from an exhaust port 15. In addition, it is the mean flow-time in the oxidative degradation of this hydrazine for 0.1 – 5 minutes, and reaction temperature is usually 30–80 degrees C.

[0039] In a vapor-liquid mixed phase reaction as shown in the example of oxidation treatment of the water containing the above-mentioned hydrazine, long duration maintenance of the catalytic activity of the catalyst particle of this invention is carried out very much. That is, although the catalytic activity of the time of reaction initiation falls very much for a short time by the particle which formed the metal oxide layer in front faces, such as a glass bead, and formed the direct metal layer in the front face of the particle which prepared the metal layer on this metal oxide layer, or a resin particle, without using a resin particle as a core material, the catalyst particle of this invention has many which catalytic activity cannot fall easily and have twice [ more than ] as many catalytic activity as the above particles.

[0040] The catalyst particle of this invention does so effectiveness equivalent to the above-mentioned example not only in oxidation treatment of a hydrazine but in various vapor-liquid mixed phase reactions. In above-mentioned drawing 2 , for example, instead of the treated water containing a hydrazine Hydrogen can be oxidized by throwing in the liquid with which hydrogen gas is dissolved in the tank 11. Moreover, reforming of the petroleum for fuel cells can be performed by throwing in the petroleum raw material for fuel cells. By throwing in the seawater where the carbon dioxide is furthermore dissolved, immobilization and reforming of a carbon dioxide can be performed, and this gas can be oxidized by throwing in the liquid which absorbed gas with the gas absorption scrubber.

[0041] Moreover, the absorption and oxidation of gas in this wetted wall column can be performed to coincidence by forming the wall material of a wetted wall column using the catalyst particle of this invention. Furthermore, the catalyst particle of this invention usually has about three 1.2 – 2.5 g/cm specific gravity, and since it approximates with the specific gravity of processing liquid, for example, in case this specific gravity uses this catalyst by the moving bed or the fluid bed in a vapor-liquid mixing phase style, it can contact a catalyst particle and processing liquid effectively.

---

## DESCRIPTION OF DRAWINGS

---

[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is the sectional view showing typically the cross-section configuration of the catalyst particle of this invention.

[Drawing 2] Drawing 2 is drawing showing typically the example of the processor of the hydrazine content water which used the catalyst particle of this invention.

**[Description of Notations]**

1 ... Core material

2 ... Metal oxide layer

3 ... Metal layer

11 ... Tank

12 ... Pump

13 ... Processor

14 ... Blois

15 ... Exhaust port





(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平7-24328

(43) 公開日 平成7年(1995)1月27日

(51) Int.Cl.<sup>8</sup>

識別記号

庁内整理番号

F I

技術表示箇所

B 0 1 J 31/06

M 8017-4G

C 0 2 F 1/72

Z 9045-4D

審査請求 未請求 請求項の数7 O L (全7頁)

(21) 出願番号

特願平5-168138

(22) 出願日

平成5年(1993)7月7日

(71) 出願人 000202350

綜研化学株式会社

東京都豊島区高田3丁目29番5号

(72) 発明者 今井達裕

埼玉県狭山市上広瀬130番地 綜研化学株式会社研究所内

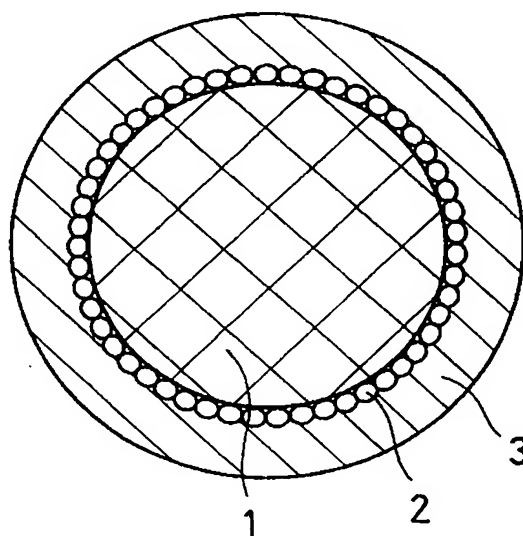
(74) 代理人 弁理士 鈴木 俊一郎

(54) 【発明の名称】 触媒粒子およびその使用方法

(57) 【要約】

【構成】 本発明の触媒粒子は、芯材である粒子径0.05～5mmの樹脂粒子と、この芯材の表面に形成された金属酸化物層と、この金属酸化物層の表面に形成された厚さ0.01～5μmの金属層とからなり、この樹脂粒子と金属酸化物層を形成する金属酸化物との重量比が99.9:0.1～90:10の範囲内にあり、そして、金属層が、パラジウム、白金、ニッケル、銅および少なくとも一種の該金属を主成分とする合金よりなる群から選ばれる金属成分を含有する。さらに本発明は、この触媒粒子を使用する方法をも提供する。

【効果】 本発明の触媒粒子は、特に気液混相反応における触媒として適しており長時間その触媒活性が低下しないとの効果を有する。



## 【特許請求の範囲】

【請求項 1】 芯材である粒子径 0.05～5mm の樹脂粒子と、該芯材の表面に形成された金属酸化物層と、該金属酸化物層の表面に形成された厚さ 0.01～5 $\mu$ m の金属層とからなり、該樹脂粒子と金属酸化物層を形成する金属酸化物との重量比が 99.9:0.1～90:10 の範囲内にあり、そして、該金属層が、パラジウム、白金、ニッケル、銅および少なくとも一種類の該金属を主成分とする合金よりなる群から選ばれる金属成分を含有することを特徴とする触媒粒子。

【請求項 2】 芯材がアクリル系樹脂粒子であることを特徴とする請求項第 1 項記載の触媒粒子。

【請求項 3】 金属酸化物が 4 価金属の酸化物であることを特徴とする請求項第 1 項記載の触媒粒子。

【請求項 4】 金属酸化物が、酸化スズ、酸化ケイ素、酸化チタンおよび酸化ジルコニウムよりなる群から選ばれる少なくとも一種類の金属酸化物であることを特徴とする請求項第 1 項または第 3 項記載の触媒粒子。

【請求項 5】 金属層が、無電解メッキ法により形成された層であることを特徴とする請求項第 1 項記載の触媒粒子。

【請求項 6】 芯材である粒子径 0.05～5mm の樹脂粒子と、該芯材の表面に形成された金属酸化物層と、該金属酸化物層の表面に形成された厚さ 0.01～5 $\mu$ m の金属層とからなり、該樹脂粒子と金属酸化物層を形成する金属酸化物との重量比が 99.9:0.1～90:10 の範囲内にあり、そして、該金属層が、パラジウム、白金、ニッケル、銅および少なくとも一種類の該金属を主成分とする合金よりなる群から選ばれる金属成分を含有する触媒粒子の存在下に、気液混相系で、反応を行うことを特徴とする触媒粒子の使用法。

【請求項 7】 気液混相系における反応が、水処理における酸化反応、水素または窒素化合物の酸化処理、溶存二酸化炭素の固定反応、燃料電池用石油の改質、または、溶存ガスの酸化処理反応のいずれかであることを特徴とする請求項第 6 項記載の触媒粒子の使用法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、粒状の形態を有する新規な触媒粒子およびこの使用方法に関する。さらに詳しくは本発明は、気液混相反応のように異なる相間での反応に特に好適な触媒粒子およびこの使用方法に関する。

## 【0002】

【発明の技術的背景およびその問題点】化学反応には、気相反応、液相反応、気液混相反応等の種々の相の反応があり、工業的には、多くの場合、反応を効率的に行うため触媒が用いられている。こうした触媒を用いた反応の内、固体触媒を用いる不均一触媒反応では、反応原料と触媒との接触性によって反応速度等が著しく変動する。

【0003】一般に、化学反応は触媒と反応原料との接触の程度が高い程全体の反応速度が大きくなることから、多孔質物質に触媒を担持させて、触媒と反応原料との接触面積を大きくしている。こうした方法は、気相反応、液相反応で非常に有効であり、既にシリカ、アルミナ等数多くの多孔質担体が用いられている。

【0004】しかしながら、気液混相反応のように反応系に気相と液相とが混在する系における反応では、気泡の表面張力のために多孔質担体の深部にまで反応原料が侵入しないために、上記のような多孔質担体を用いて単位体積当たりの表面積を大きくしても、触媒粒子内部へ気相の拡散が妨害され全体の反応速度はそれほど改善されない。例えば特開昭58-122046号、同62-38245号公報等には気液混相反応で使用する触媒に撥水性多孔質担体を使用して、水滴で孔口が閉塞されないようにして、反応性を確保した気液混相反応における触媒が開示されており、こうした提案から明らかなように、気液混相反応における触媒の反応性は、一般的な触媒のように単に比表面積を高くすることによっては改善されない。

【0005】近年、CODまたはBOD値を低減させるため溶存物質を酸化処理し、環境汚染の低減を図ろうとする要請が強くなり、一般水処理等においてさえも酸化処理した後に排水することが必要になってきている。こうした一般水処理における酸化処理では気液混相反応が利用されており、しかもこの気液混相反応で著しく多量の水を処理する必要がある。従って、こうした気液混相反応では、より活性の高い触媒を使用することが必要であるとともに、さらにその活性をできるだけ長時間維持することが必要になる。

【0006】こうした気液混相系における反応の触媒として、例えば、特開平4-166215号公報には、電気式脱イオン水製造装置から排出される電極水の処理方法の発明が開示されている。

【0007】この方法では、イオン交換樹脂にパラジウムを担持させた触媒の存在下に、水素ガスを含む陰極水と酸素ガスを含有する陽極水とを接触させることにより水素ガスと酸素ガスを反応させて水処理を行っている。

【0008】このような水処理では、非常に多量の水を処理しなければならず、さらにパラジウムが高価であることから、触媒の活性をできるだけ長時間維持する必要がある。

【0009】また、気液混相反応における反応性を向上させるために、反応系における気液混合状態を改善する方法等、種々の提案がある（特開昭53-110968号、同63-252540号、特開平3-196832号、同4-156937号等の公報参照）。しかしながら、これらの公報には、触媒自体の構造を変えて反応性を改善しようとする試みは開示されていない。

【0010】ところで、樹脂からなる芯材としてこの芯

3、

材上に無電解メッキ法で金属層を形成する際に、芯材の濡れ性を向上させるために芯材上に金属酸化物層を形成する方法およびこのような構造を有する金属被覆粒子は既に知られている（例えば特開平4-228503号、同4-183804号公報参照）。

【0011】しかしながら、これらの公報において、金属酸化物層は、金属層を形成する際の芯材の濡れ性を改善するために設けられているのであり、さらにこれらの金属被覆粒子は塗料、接着剤、粉末冶金、射出成形、電磁波シールド材、分散強化材、静電複写トナー、粉体塗料および化粧料等としての使用が提案されているだけであり、触媒としての用途に関しては全く検討されていない。

【0012】本発明者はこうした金属被覆粒子について従来全く検討されていなかった触媒の分野において種々検討を行った結果、樹脂芯材表面に金属酸化物層を介して特定の金属から形成された金属層を有する粒子が優れた触媒作用を有すると共に、その触媒作用が長期間維持されるとの知見を得て本発明を完成するに至った。

【0013】

【発明の目的】本発明は、新規な形態の触媒粒子およびその触媒粒子を使用する方法を提供することを目的とする。さらに詳しくは本発明は、触媒活性が低下しにくく長時間使用することができる触媒粒子およびこの触媒粒子を使用する方法を提供することを目的としている。

【0014】

【発明の概要】本発明の触媒粒子は、芯材である平均粒子径0.05～5mmの樹脂粒子と、該芯材の表面に形成された金属酸化物層と、該金属酸化物層の表面に形成された厚さ0.01～5μmの金属層とからなり、該樹脂粒子と金属酸化物層を形成する金属酸化物との重量比が99.9:0.1～90:10の範囲内にあり、そして、該金属層が、パラジウム、白金、ニッケル、銅および少なくとも一種の該金属を主成分とする合金よりなる群から選ばれる金属成分を含有することを特徴としている。

【0015】また、本発明の触媒粒子の使用方法は、芯材である平均粒子径0.05～5mmの樹脂粒子と、該芯材の表面に形成された金属酸化物層と、該金属酸化物層の表面に形成された厚さ0.01～5μmの金属層とからなり、該樹脂粒子と金属酸化物層を形成する金属酸化物との重量比が99.9:0.1～90:10の範囲内にあり、そして、該金属層が、パラジウム、白金、ニッケル、銅および少なくとも一種の該金属を主成分とする合金よりなる群から選ばれる金属成分を含有する触媒粒子の存在下に、気液混相系で、反応を行うことを特徴としている。

【0016】本発明の触媒粒子は、上記のように樹脂粒子の表面に金属酸化物層および金属層がこの順序で積層された断面構造を有する。このように芯材の表面に金属酸化物からなる薄層を形成し、さらにこの金属酸化物層

4

の上に金属層を形成することにより、触媒活性が経時的に低下しにくくなる。

【0017】また、芯材として樹脂粒子を使用しているので、この触媒粒子の比重が低くなり、移動層または流動層のようにこの触媒を固定しないで使用する場合には、反応系に対する分散が非常に容易になる。

【0018】特に本発明の触媒粒子は、気液混相系における反応触媒、気液混相反応、さらに詳しくは原料系または生成系の少なくとも一方が気体または液体である気液混相反応における触媒として有用性が高い。

【0019】

【発明の具体的説明】次に本発明の触媒粒子およびその使用方法について具体的に説明する。本発明の触媒粒子は、図1に示すように、芯材1、この芯材1表面に形成された金属酸化物層2、および、この金属酸化物層2上に形成された金属層3からなる。

【0020】本発明の触媒粒子において、芯材は樹脂から形成されている。この芯材は、0.05～5mmの範囲内の平均粒子径を有しており、さらに0.1～5mmの平均粒子径を有する樹脂粒子が好ましく、0.2～2mmの平均粒子径を有する樹脂粒子が特に好ましい。上記のような平均粒子径を有する樹脂粒子は、曲率半径があまり小さくならないので、この樹脂粒子表面に均一な金属層を例えば無電解メッキ法で容易に形成することができる。

【0021】この芯材を形成する樹脂の例としては、（メタ）アクリル系樹脂、スチレン系樹脂、スチレン／（メタ）アクリル系樹脂、ポリエチレン系樹脂、ポリプロピレン系樹脂、ABS樹脂、AS樹脂、ポリアセタール樹脂、ポリカーボネート系樹脂、フェノール系樹脂、ベンゾグアナミン系樹脂、エポキシ系樹脂、ポリエステル系樹脂、ポリアミド系樹脂、ウレタン系樹脂およびポリイミド系樹脂を挙げることができる。この有機重合体は、架橋重合体または非架橋重合体のいずれであってもよい。これらの中でも（メタ）アクリル系樹脂（例：メチルメタクリレート）およびスチレン／（メタ）アクリル系樹脂のようなアクリル系樹脂が好ましい。

【0022】このように芯材として樹脂粒子を用いることにより、本発明の触媒粒子の比重が低くなり反応系への分散が容易になると共に、例えば芯材としてガラスビーズなど用いた場合よりも触媒活性を長時間維持することができる。

【0023】本発明の触媒粒子には、上記のような芯材表面に金属酸化物層が形成されている。この金属酸化物層は、通常は4価金属の酸化物から形成されており、このような4価金属の酸化物の好適な例としては、酸化スズ、酸化ケイ素、酸化チタンおよび酸化ジルコニウムを挙げることができる。ここで金属酸化物としては、通常は0.001～1μm、好ましくは0.02～0.1μmの平均粒子径を有する粒子が使用される。すなわち、通

常、芯材である樹脂粒子の  $1/5,000,000 \sim 1/50$  程度、好ましくは  $1/10,000 \sim 1/5,000$  程度の平均粒子径を有する金属酸化物粒子が使用される。

【0024】この金属酸化物層は、樹脂粒子と金属酸化物粉末とを、ボールミル等の混合機を用いて乾式混合法（ドライブレンド法、メカノケミカル法）により形成することができる。ここで乾式混合法の例としては、ハイブリダイゼーションシステム（株式会社奈良機械製作所製）、メカノフュージョンシステム（ホソカワミクロン株式会社製）、コスモス（川崎重工業株式会社製）等の粒子複合化装置を用いた方法を挙げることができる。このような乾式混合法で樹脂粒子と金属酸化物粒子とを混合することにより樹脂粒子表面に連続性の高い金属酸化物層を形成することができる。

【0025】さらに、樹脂と金属酸化物を不均一に溶融混練し、その後に粉碎すると金属酸化物が表面に固定された樹脂粒子が得られる。上記の方法の他、金属酸化物が水およびモノマーに不溶もしくは難溶の場合には、この金属酸化物粒子を水性溶媒に分散させ、この水性溶媒中にモノマーを入れて懸濁重合することにより、金属酸化物が分散安定剤として作用するため、重合させながら表面に金属酸化物が固定された樹脂粒子が得られる。このように重合させることにより、金属酸化物は、その界面作用により殆どが樹脂粒子表面に薄層を形成して固定され、均一な金属酸化物層を形成する。

【0026】特に本発明では粒子複合化装置で形成された金属酸化物層、および、懸濁重合の際に金属酸化物を配合して重合させることにより形成された金属酸化物層が好ましい。

【0027】このように樹脂芯材上に金属酸化物層を介して金属層を形成することにより、触媒活性を長時間維持することができる。しかも例えば無電解メッキ法により均一性の高い金属層を容易に形成することができる。

【0028】本発明の触媒粒子は、上記の金属酸化物層上に金属層を有している。この金属層は、触媒作用を有する金属により形成されており、金属酸化物層における金属とは別の金属である。

【0029】このような触媒作用を有する金属として、パラジウム、白金、ニッケル、銅およびこれらの金属を主成分として含有する合金を挙げることができる。すなわち、この金属層は、パラジウム、白金、ニッケルまたは銅のいずれかの金属単独で形成されていてもよいし、これらの金属の合金であってもよい。さらに、この金属層には、触媒作用が損なわれない範囲内で、他の成分が含有されていてもよい。ここで、上記金属または合金と共に金属層を形成することができる他の成分の例としては、B、P、Co、Fe、Ag、Au、Rh、Ru、Cr、Cd、Pb、Sn、Zn、W、In および Ir を挙げることができる。このような他の成分は、金属層に通常は 25 重量%以下、好ましくは 13 重量%以下、さら

に好ましくは 4 重量%以下の量で含有されることができる。

【0030】この金属層は、例えば真空蒸着法、スパッタリング法、PVD および CVD 法等により形成することができるが、特に本発明では無電解メッキ法により形成することが好ましい。

【0031】無電解メッキ法は、金属イオンを含有する水溶液に還元剤を加えて加温乃至加熱することにより電流を流すことなく金属を析出させる方法であり、この無電解メッキ法により形成された金属層は非常に均一性が高くなる。

【0032】金属層は、 $0.01 \sim 5 \mu\text{m}$  の平均層厚を有しており、さらにこの平均層厚が  $0.1 \sim 1.5 \mu\text{m}$  の範囲内にあることが好ましい。また、この金属層を形成する金属と前記金属酸化物層を形成する金属酸化物との重量比は  $99.9:0.1 \sim 90:10$  の範囲内にある。金属と金属酸化物とを上記のような量で用いることにより、触媒の活性が長時間維持される。

【0033】この金属層は、前述のようにして芯材の表面に金属酸化物層を形成した後、通常は感応化処理および活性化処理を施し、次いで無電解メッキ法により金属層を形成する。ここで感応化処理は被メッキ物を塩化第 1 スズ塩酸溶液等に浸漬する処理であり、活性化処理は感応化処理した被メッキ物を塩化パラジウム塩酸溶液等に浸漬する処理である。

【0034】こうして感応化処理および活性化処理が施された被メッキ体、即ち金属酸化物層が形成された芯材を、室温  $\sim 90^\circ\text{C}$  の範囲内の温度に維持された無電解メッキ液中に投入して、攪拌下に 10 分  $\sim 24$  時間反応させることにより、金属層を形成することができる。

【0035】本発明の触媒粒子は、上記のように芯材として樹脂粒子を用いているので、比重が低くなり、反応系への触媒粒子の分散が容易になる。さらにこのように芯材として樹脂粒子を用い、さらに金属酸化物層を介して触媒となる金属層を形成することにより、触媒粒子の活性を長時間維持することができる。本発明の触媒粒子において触媒活性の低下が少なく、その活性が長時間維持されることについての機構は明確ではないが、後述するように実施例と比較例との対比から明らかなように、樹脂芯材および金属酸化物層が互いに共同することにより触媒活性が低下しにくくなっていることがわかる。

【0036】本発明の触媒粒子は、表面にある金属層を形成する金属の種類によって種々の反応に対する触媒活性を有し、液相反応、気相反応のような単一相での触媒、特に酸化触媒として使用することができるが、特に異なる相間で進行する反応の触媒として好適である。このような異なる相間で進行する反応の例としては、原料系または生成系の少なくとも一方が気体または液体である気液混相反応を挙げることができる。さらに本発明の触媒粒子は、このような気液混相反応における酸化触媒

として有用性が高い。

【0037】こうした気液混相反応の例としては、水処理における酸化反応、水素または窒素化合物の酸化処理、溶存二酸化炭素の固定反応、燃料電池用石油の改質、溶存ガスの酸化処理反応、アルデヒド類の酸化反応、アルコール類の酸化反応およびアルコール類の脱水素反応を挙げることができる。これらの中でも本発明の触媒粒子は、水処理における酸化反応、水素または窒素化合物の酸化処理、溶存二酸化炭素の固定反応、燃料電池用石油の改質および溶存ガスの酸化処理反応における酸化触媒としての有用性が高い。

【0038】図2に窒素化合物であるヒドラジンを含有する水の酸化処理の例を示す。タンク11からヒドラジンを含有する処理水を送液ポンプ12で下端部から処理塔13に導入する。これとは別に空気をブロー14で同様に処理塔13の下端部から導入し、処理塔13内で処理水と空気とを混合する。この処理塔13内には、アクリル系樹脂芯材の表面に酸化ケイ素層およびパラジウム層がこの順序で積層された本発明の触媒粒子が充填されており、この触媒粒子と前記処理水および空気とは気液混相状態で接触する。この処理水と空気とは上昇流で触媒粒子と接触することが好ましい。このように処理することにより、ヒドラジンは酸化分解されて窒素と水となり、排水口15から排出される。なお、このヒドラジンの酸化分解における平均滞留時間は通常は0.1～5分間、反応温度は通常は30～80℃である。

【0039】上記ヒドラジンを含有する水の酸化処理の例で示すような気液混相反応において、本発明の触媒粒子の触媒活性は非常に長時間維持される。すなわち、芯材として樹脂粒子を使用せずに、例えばガラスビーズ等の表面に金属酸化物層を形成し、この金属酸化物層上に金属層を設けた粒子、または、樹脂粒子の表面に直接金属層を形成した粒子等では、反応開始当初の触媒活性が非常に短時間で低下するが、本発明の触媒粒子は触媒活性が低下しにくく、上記のような粒子の2倍以上の触媒能力を有するものが多い。

【0040】本発明の触媒粒子は、ヒドラジンの酸化処理に限らず、種々の気液混相反応において上記の例と同等の効果を奏する。例えば上記図2において、ヒドラジンを含有する処理水の代わりに、タンク11内に水素ガスが溶存している液を投入することにより水素を酸化処理することができ、また燃料電池用石油原料を投入することにより燃料電池用石油の改質を行うことができ、さらに二酸化炭素が溶存している海水を投入することにより二酸化炭素の固定・改質を行うことができ、ガス吸収スクラバーでガスを吸収した液を投入することによりこのガスを酸化処理することができる。

【0041】また、本発明の触媒粒子を用いて濡れ壁塔の内壁材を形成することにより、この濡れ壁塔におけるガスの吸収および酸化を同時に行うことができる。さら

に、本発明の触媒粒子は、通常1.2～2.5g/cm<sup>3</sup>程度の比重を有しており、この比重は処理液の比重と近似しているため、例えばこの触媒を気液混合相流における移動層もしくは流動層で使用する際に触媒粒子と処理液とを有効に接触させることができる。

【0042】

【発明の効果】本発明の触媒粒子では、樹脂粒子からなる芯材およびこの芯材表面に金属酸化物層を有し、この金属酸化物層の上に金属層が形成されているので、異なる相が相接する相間における反応、特に気液混相における酸化反応において、有効な触媒活性が長期期間維持される。

【0043】また、この触媒粒子は、芯材が樹脂粒子からなるので、比重が低く、反応させようとする液体と近似した比重を有する。従って、例えば本発明の触媒粒子を用いることにより、処理物質と触媒粒子とを有効に接触させることができる。

【0044】本発明の触媒粒子は、特に気液混相における反応触媒として有用性が高い。

【0045】

【実施例】次に実施例を示して本発明を説明するが、本発明はこれにより限定されるものではない。

【0046】

【製造例1】攪拌装置、温度計および窒素ガス導入管を有するステンレス製の容量5リットルの重合容器中に、水1400重量部を仕込んだ。次いでこの水にポリビニルアルコール3.3重量部を溶解させた後、この溶液にベンゾイルパーオキサイド6重量部を溶解させたメチルメタクリレート600重量部を添加し、ゆっくりとした一定の攪拌条件下で75℃で5時間加熱し、懸濁重合を完了させた。

【0047】得られた懸濁液を、遠心脱水後、水洗乾燥して平均粒子径200μmのポリメチルメタクリレート粉体を得た。

【0048】

【製造例2】製造例1において、水1400重量部の代わりに、水1400重量部および酸化ケイ素18重量部を仕込んだ以外は同様にして懸濁重合を行い、平均粒子径200μmの粉体を得た。

【0049】得られた粉体を走査型電子顕微鏡で観察したところ、粒子表面が酸化ケイ素で被覆されたポリメチルメタクリレート粉体であった。

【0050】

【製造例3】製造例1で得られたポリメチルメタクリレート粉体100gと酸化ケイ素3gとを市販の容量500ccポリ瓶に入れ、ポリ瓶の回転数が60ppmになるように回転速度を調節し、60分間処理した。

【0051】得られた粉体を走査型電子顕微鏡で観察したところ、製造例1で得られたのと同様の酸化ケイ素で被覆されたポリメチルメタクリレート粉体であった。

## 【0052】

【比較例1】製造例1で得られた粉体を塩化第1すず塩酸溶液に浸漬し、感応化処理を施した後、塩化パラジウム塩酸溶液に浸漬し、活性化処理を施した。

【0053】次いで、処理粉体50gを、塩化パラジウム32g、25%アンモニア水400g、エチレンジアミン四酢酸二ナトリウム68g、ヒドラジン5.8gおよびイオン交換水600gからなるメッキ液で、40℃で1時間かけて無電解メッキを行った。その後、遠心脱水し、水洗乾燥してパラジウムメッキ粒子を得た。得られたメッキ粒子のパラジウム層の厚さは、1.1μmであ

った。

【0054】得られた粉体を用いて、図2に示すヒドラジン分解能測定装置により、ヒドラジンの分解速度を測定したところ、表1に示すように、反応開始直後のヒドラジン分解速度は高かったが、触媒活性が短時間で低下して24時間経過後では実用的に有効な触媒活性は示さなくなった。結果を表1に示す。

## 【0055】

【実施例1】製造例2で得られた粉体を塩化第1すず塩酸溶液に浸漬し、感応化処理を施した後、塩化パラジウム塩酸溶液に浸漬し、活性化処理を施した。

【0056】次いで、処理粉体50gを、塩化パラジウム32g、25%アンモニア水400g、エチレンジアミン四酢酸二ナトリウム68g、ヒドラジン5.8gおよびイオン交換水600gからなるメッキ液で、40℃で1時間かけて無電解メッキを行った。

【0057】その後、遠心脱水し、水洗乾燥してパラジウムメッキ粒子を得た。得られたメッキ粒子のパラジウム層の厚さは、1.1μmであった。得られた粉体を用いて、図2に示すヒドラジン分解能測定装置により、ヒドラジンの分解速度を測定したところ、表1に示すよう

に、24時間経過の触媒活性と28日経過後の触媒活性との間に殆ど差がなく、長期間この触媒を使用することができた。結果を表1に示す。

## 【0058】

【実施例2】製造例3で得られた粉体を塩化第1すず塩酸溶液に浸漬し、感応化処理を施した後、塩化パラジウム塩酸溶液に浸漬し、活性化処理を施した。

【0059】次いで、処理粉体50gを、塩化パラジウム32g、25%アンモニア水400g、エチレンジアミン四酢酸二ナトリウム68g、ヒドラジン5.8gおよびイオン交換水600gからなるメッキ液で、40℃で1時間かけて無電解メッキを行った。

【0060】その後、遠心脱水し、水洗乾燥してパラジウムメッキ粒子を得た。得られたメッキ粒子のパラジウム層の厚さは、1.1μmであった。得られた粉体を用いて、図2に示すヒドラジン分解能測定装置により、ヒドラジンの分解速度を測定したところ、表1に示すように、24時間経過の触媒活性と28日経過後の触媒活性との間に殆ど差がなく、長期間この触媒を使用することができた。結果を表1に示す。

## 【0061】

【比較例2】実施例1において、製造例2で得られた粉体の代わりに、市販のガラスビーズ（平均粒子径0.2mm）を用いた以外は同様にして触媒粒子を製造した。

【0062】この触媒粒子を用いて実施例1と同様にしてヒドラジンの分解速度を測定したが、反応開始直後の分解速度もそれほど高くはなく、さらに24時間後には比較例1の分解速度以下になったので、この段階で反応を中止した。結果を表1に示す。

## 【0063】

## 【表1】

表 1

	ヒドラジン分解速度 (mg/min/cc-触媒)		
	開始直後	24 時間後	28 日後
比較例 1	0.42	0.05	0.05
実施例 1	0.29	0.13	0.12
実施例 2	0.29	0.13	0.12
実施例 3	0.31	0.12	0.11
比較例 2	0.20	0.04	—

## 【図面の簡単な説明】

【図 1】 図 1 は本発明の触媒粒子の断面形状を模式的に示す断面図である。

【図 2】 図 2 は本発明の触媒粒子を用いたヒドラジン含有水の処理装置の例を模式的に示す図である。

## 【符号の説明】

1 … 芯材

\* 2 … 金属酸化物層

3 … 金属層

11 … タンク

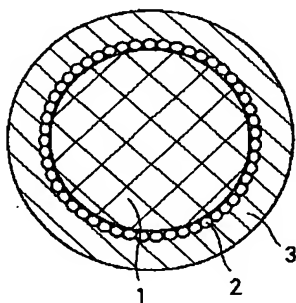
12 … ポンプ

13 … 処理装置

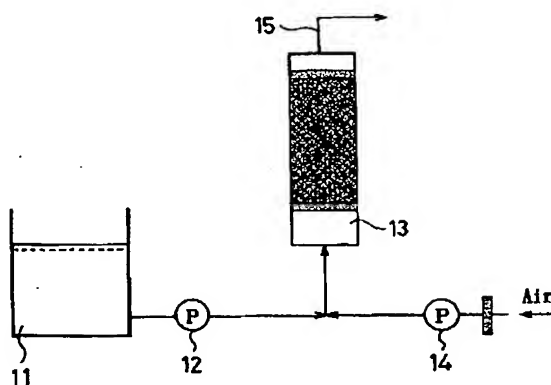
14 … プロア

\* 15 … 排出口

【図 1】



【図 2】



This Page Blank (uspto)